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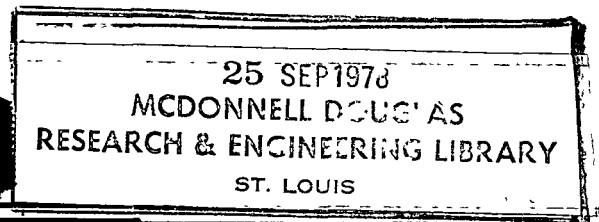
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CORROSION INHIBITORS FOR SOLAR HEATING AND COOLING SYSTEMS

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For the U. S. Department of Energy

August 1978



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Solar Energy

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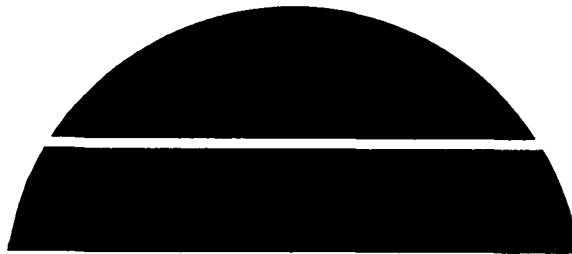
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TABLE OF CONTENTS

| | Page |
|----------------------------------|------|
| INTRODUCTION | 1 |
| TEST PROCEDURE | 1 |
| RESULTS AND DISCUSSION | 3 |
| CONCLUSIONS | 4 |
| REFERENCES | 10 |

LIST OF ILLUSTRATIONS

| Figure | Title | Page |
|--------|------------------------------------------------|------|
| 1. | Test assembly and method of exposure | 8 |
| 2. | Appearance of test specimens | 9 |

LIST OF TABLES

| Table | Title | Page |
|-------|-------------------------------------------------------------|------|
| 1. | Composition of Corrosion Inhibitors (grams/liter) | 5 |
| 2. | Corrosion Test Data | 6 |
| 3. | Rating of the Corrosion Inhibitors | 7 |

CORROSION INHIBITORS FOR SOLAR HEATING AND COOLING SYSTEMS

INTRODUCTION

A program was initiated to evaluate corrosion inhibitors for solar heating and cooling (SHAC) systems. Most of these systems will probably consist of components made from aluminum, mild steel, copper and stainless steel, and the dissimilar metals may well be in electrical contact. Water or antifreeze solutions will be used for heat transfer and heat storage. If the system will be used for cooling, part of the unit will be operated at a relatively high temperature (90° to 95°C). The problem of corrosion protection will probably be complicated further by a prohibition against the use of toxic or polluting chemicals.

Three inhibitors showed promise in the initial investigation [1] and these inhibitors were included in this test to verify the original performance. Several additional inhibitors including four proprietary products were also tested. These four products were supplied by commercial producers of corrosion inhibitors for water systems. The original test was conducted at room and elevated temperature in corrosive water and a permanent type antifreeze, but this investigation was limited to corrosive water at elevated temperature.

TEST PROCEDURE

The inhibitors consisted primarily of the ones that appeared promising in the initial test, plus several proprietary products. According to the manufacturers, the proprietary products are considered nontoxic and nonpolluting in small amounts; this is also true of the other test inhibitors. The composition of the formulated inhibitors and the names and concentrations of the proprietary products are given in Table 1.

Small 2.5 by 7.5 cm specimens were sheared from sheets of 1100 aluminum, 1010 steel, and 321 stainless steel; 1.9 by 7.5 cm specimens were sheared from electrolytic tough pitch copper. All the materials were in the annealed condition except the 1100 aluminum which was in the H14 temper. The sheet thicknesses ranged from 1.2 mm for the aluminum to 2.0 mm for the copper and stainless steel. All the specimens were deburred and cleaned

in a hot alkaline bath (aluminum in Enbond NE-6 and the others in Enbond S-64). The aluminum specimens were etched in a 10 percent nitric acid-2 percent hydrofluoric acid solution and desmutted in 40 percent nitric acid. The mild steel and stainless steel specimens were cleaned in 20 percent hydrochloric acid, and the copper specimen was cleaned in 40 percent nitric acid.

Test assemblies were made by drilling a small hole in one end of each specimen, inserting an 18-8 stainless steel machine screw through the hole in the 1100 aluminum alloy specimen, and securing it with a stainless steel nut. Steel, copper, and stainless steel specimens were added in sequence to the screw, and a stainless steel nut secured finger tight was placed between each specimen to act as a separator and to insure electrical contact (Fig. 1).

The assemblies were immersed in 450 ml of the respective solutions contained in 500 ml Erlenmeyer flasks covered with loosely fitting glass stoppers and placed in a hot (82°C) water bath. All the test assemblies were removed from the solutions and placed in empty covered flasks each working day for 8 hours. This procedure was used to simulate a system drained at night during the winter to prevent freezing. The specimens were visually inspected each working day, and the solution level was maintained by additions of distilled water to insure constant solution concentration. After one year of exposure, the assemblies were removed, disassembled, cleaned, and weighed. The specimens were cleaned according to ASTM G1-72, "Preparing, Cleaning, and Evaluating Corrosion Test Specimens," paragraphs 5.1, 5.2, 5.7.2, and 5.8.2.

The procedure used in this test was similar to that used in the original test program so as to produce comparable results. One difference was that this test was conducted in duplicate. Although the specimen length and width were the same, the thickness of the aluminum was 1.2 mm instead of 3.1 mm and the steel was 1.6 mm instead of 0.9 mm. The same type of corrosive water was used and was composed of 148 ppm sodium sulfate, 165 ppm sodium chloride, and 138 ppm sodium bicarbonate (100 ppm each sulfate, chloride, and bicarbonate) per ASTM D1384-70, "Corrosion Test for Engine Coolants in Glassware," paragraph 6. Only elevated temperature (82°C) tests were employed because all SHAC systems are operated at elevated temperature, and the results of the initial test indicated that elevated temperature was normally a more severe test than room temperature.

RESULTS AND DISCUSSION

Since perforation of SHAC components will make the system inoperative, the type and depth of attack were the major factors used in the corrosion evaluation. The appearance of the aluminum and steel specimens is shown in Figure 2, and a description of the conditions and other test data are given in Table 2. Results on copper and stainless steel are not shown because the copper specimens were only mildly etched (maximum calculated corrosion rate of less than 0.002 mm/yr) and the stainless steel specimens were unaffected. Weight loss is included in Table 2, but its use was limited to rating specimens for which the general pattern of attack was similar and the frequency of pitting was approximately the same.

Evaluation of the corrosion inhibitors was based on the corrosion protection afforded aluminum and mild steel because neither copper nor stainless steel suffered significant corrosion in any of the solutions, including the uninhibited water. The inhibitors are rated in Table 3 by placing them in three categories according to protection afforded aluminum, protection afforded mild steel, and protection afforded a combination of the two. The reason for the three categories is that either material may be corrosion critical in some systems, but in many systems both materials may be corrosion critical and the inhibitor must protect aluminum and steel equally.

The performance of Inhibitors 1 and 2 agrees very well with the results obtained in the previous test. However, the performance of Inhibitors 3 and 5 does not agree with the previous test, especially in protecting the aluminum. Both inhibitors protected the aluminum specimens in the initial test, but the aluminum specimens suffered severe edge attack in this test. The severe edge attack of the aluminum specimens is evident on Specimens 3 and 5 of Figure 2. The fact that the aluminum specimens did not suffer any significant edge attack in the original test but suffered severe edge attack in this test can be attributed to the difference in thickness. The aluminum used in the initial test was 3.1 mm thick, and it was possible to produce smooth rounded edges on the specimens. This was not possible on the thinner material (1.2 mm) used in this test. It is well established that sharp edges are difficult areas for corrosion protection. Metals such as aluminum that depend on natural oxide films for corrosion protection are susceptible to edge attack because the protective film does not form readily on sharp edges. For the same reason anodic and chemical conversion coatings (anodize, Alodine, Iridite) do not effectively protect sharp edges on aluminum. It may be that Inhibitors 3 and 5 will protect aluminum if there are no thin or sharp edges, but additional tests will be required for verification. The fact remains that Inhibitors 1 and 2 protected aluminum under both conditions.

One significant aspect of this test is that the most effective corrosion inhibitors for aluminum are moderately to highly alkaline (pH of 9.4 to 11.5). Another interesting aspect is the effect of reserve alkalinity on the performance of inhibitors. The only difference between Inhibitors 1 and 2 is that Inhibitor 1 contains 1.0 gram/liter of sodium hydroxide (Table 1) which was added according to L. C. Rowe of General Motors Corporation [2] to increase the reserve alkalinity. Both inhibitors protected aluminum during the test period. Inhibitor 2 protected the steel for only 1 month, whereas Inhibitor 1 protected the steel for approximately 10 months. Based on performance and the difference in pH, it appears that alkalinity is a significant factor. It is possible that the performance of this inhibitor could be improved or the service life extended by increasing the sodium hydroxide content or by periodic additions.

CONCLUSIONS

Inhibitors 1 and 6 (Table 3) are very effective inhibitors for aluminum and steel under the conditions of this test and are recommended for consideration in multimetallic solar heating and cooling systems. Although Inhibitors 3 and 5 showed promise in the previous test [1], neither inhibitor protected the aluminum component in this investigation, and additional testing is required before these two inhibitors can be recommended. For systems where aluminum components are not corrosion critical, Inhibitors 5 and 7 may give adequate protection, and Inhibitor 2 may also be considered for systems having no corrosion critical steel parts. An all stainless steel, copper, or combination system is probably the most corrosion resistant, but the cost may be prohibitive. Because of the effectiveness of Inhibitors 1 and 6 in this test, their evaluation under simulated or actual service conditions is recommended to determine their effectiveness under a variety of operating conditions and the effect of factors such as fluid flow and heat transfer.

TABLE 1. COMPOSITION OF CORROSION INHIBITORS (grams/liter)

1. 1.0 NaNO_3 , 2.0 $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 2.5 NaMBT, 3.0 $\text{Na}_2\text{B}_4\text{O}_7$, 1.0 $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, 1.0 NaOH, formulated by General Motors
2. Same as No. 1 without the NaOH
3. 1.5 NaNO_3 , 2.0 $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 2.5 NaMBT, 4.0 $\text{Na}_2\text{B}_4\text{O}_7$
4. 1.5 NaNO_2 , 2.0 $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, 2.5 NaMBT, 4.0 $\text{Na}_2\text{B}_4\text{O}_7$
5. 1.4 Na_2HPO_4 , 2.4 MBT, 6.2 $\text{Na}_2\text{B}_4\text{O}_7$: Source-15.0 Cooling System Inhibitor, Federal Specification 0-1-490A
6. 20.0 Mobay Product OC2002 — sodium benzoate base
7. 30.0 Nalco 2755
8. 1.5 Mogul WS-142
9. 5.0 Mogul WS-142
10. 5.0 Hercules CR408
11. 10.0 Hercules CR408
12. Uninhibited test water

NaNO_2 — sodium nitrite

$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ — sodium silicate

NaNO_3 — sodium nitrate

$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ — trisodium phosphate

$\text{Na}_2\text{B}_4\text{O}_7$ — sodium borate

Na_2HPO_4 — disodium phosphate

MBT — mercaptobenzothiazole

NaOH — sodium hydroxide

NaMBT — sodium mercaptobenzothiazole, 50 percent solution

TABLE 2. CORROSION TEST DATA

| Inhibitor No. | pH | | Alloy | Time (month) | Description of Corrosion | Weight Loss (mg) |
|---------------|----------|-------|-------|--------------|--------------------------|------------------|
| | Original | Final | | | | |
| 1 | 11.5 | 9.5 | Al | 12 | No visible | 2, 3 |
| 2 | 9.8 | 8.0 | Fe | 12 | Mildly rusted | 97, 98 |
| 3 | 9.4 | 8.9 | Al | 12 | No visible | 3, 4 |
| 4 | 9.5 | 9.3 | Fe | 12 | Pitted | 499, 522 |
| 5 | 9.0 | 8.5 | Al | 12 | Severe edge | 996, 1046 |
| 6 | 9.5 | 9.4 | Fe | 12 | Severe edge | 1869, 2350 |
| 7 | 9.2 | — | Al | 12 | Severe edge | 731, 997 |
| 8 | 9.7 | — | Fe | 12 | Pitted | 1015, 1264 |
| 9 | 10.2 | — | Al | 12 | Severe edge | 835, 1406 |
| 10 | 6.1 | — | Fe | 12 | Rusted | 20, 262 |
| 11 | 5.9 | — | Al | 12 | Stained | 5, 6 |
| 12 | 7.8 | — | Fe | 12 | Mildly rusted | 49, 66 |
| | | | Al | 12 | Pitted | 436, 452 |
| | | | Fe | 3-1/2 | Mildly rusted | 49, 60 |
| | | | Al | 3-1/2 | Severe edge | 700, 834 |
| | | | Fe | 3-1/2 | Pitted | 826, 919 |
| | | | Al | 3-1/2 | Severe edge | 560, 643 |
| | | | Fe | 3-1/2 | Severe edge | 754, 759 |
| | | | Al | 3-1/2 | Severe edge | 737, 1024 |
| | | | Fe | 3-1/2 | Pitted | 613, 745 |
| | | | Al | 3-1/2 | Severe edge | 586, 697 |
| | | | Fe | 3-1/2 | Severe edge | 670, 764 |
| | | | Al | 8, 12 | Severe edge | 1470, 2272 |

TABLE 3. RATING OF THE CORROSION INHIBITORS

| Al ^a | Steel ^a | Both |
|-----------------|--------------------|------|
| 1 ^b | 6 ^b | 1 |
| 2 ^b | 7 ^b | 6 |
| 6 ^b | 1 ^b | |
| 3 | 5 ^b | |
| 4 | 2 | |
| 5 | 4 | |
| 7 | 3 | |
| 9 | 10 | |
| 11 | 11 | |
| 8 | 9 | |
| 10 | 8 | |
| 12 | 12 | |

- a. The inhibitors are listed in descending order according to their effectiveness.
- b. The only inhibitors that were considered effective.

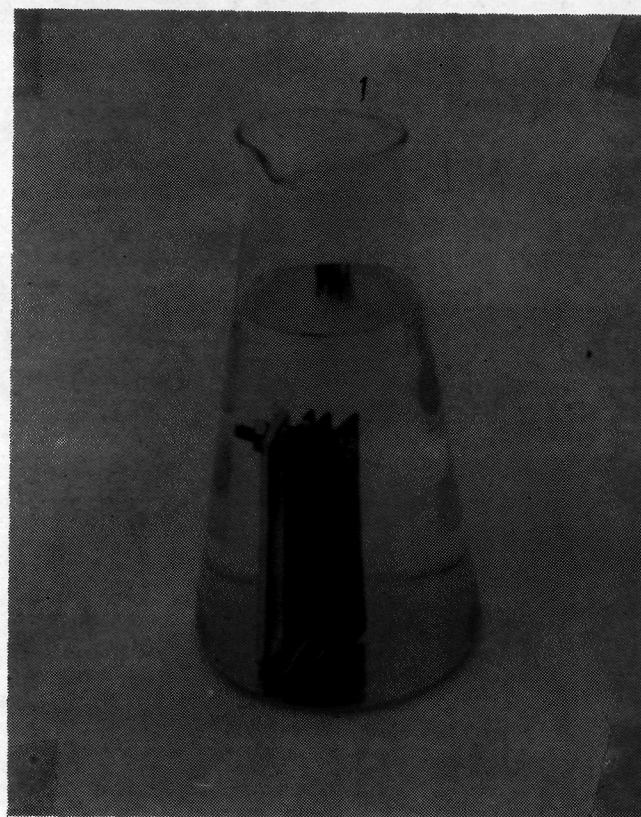
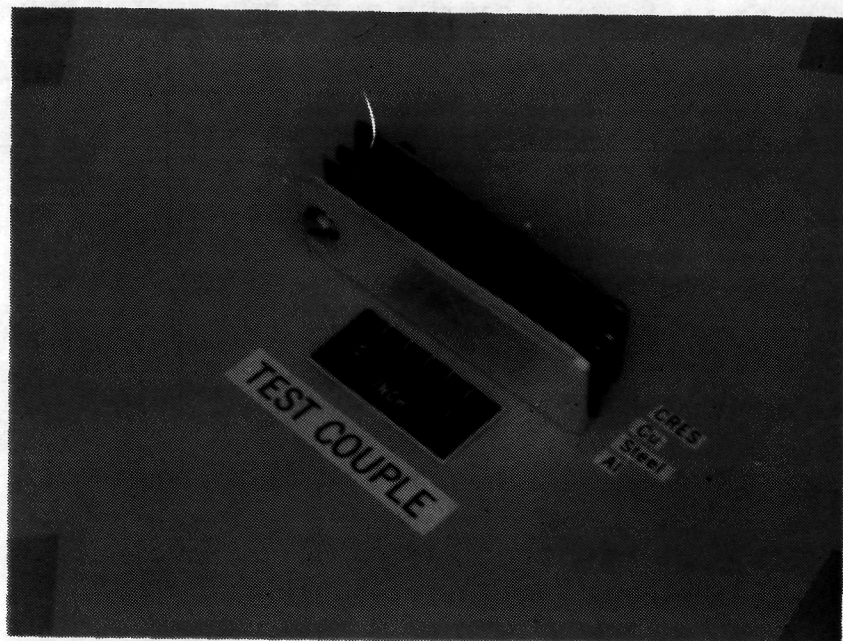


Figure 1. Test assembly and method of exposure.

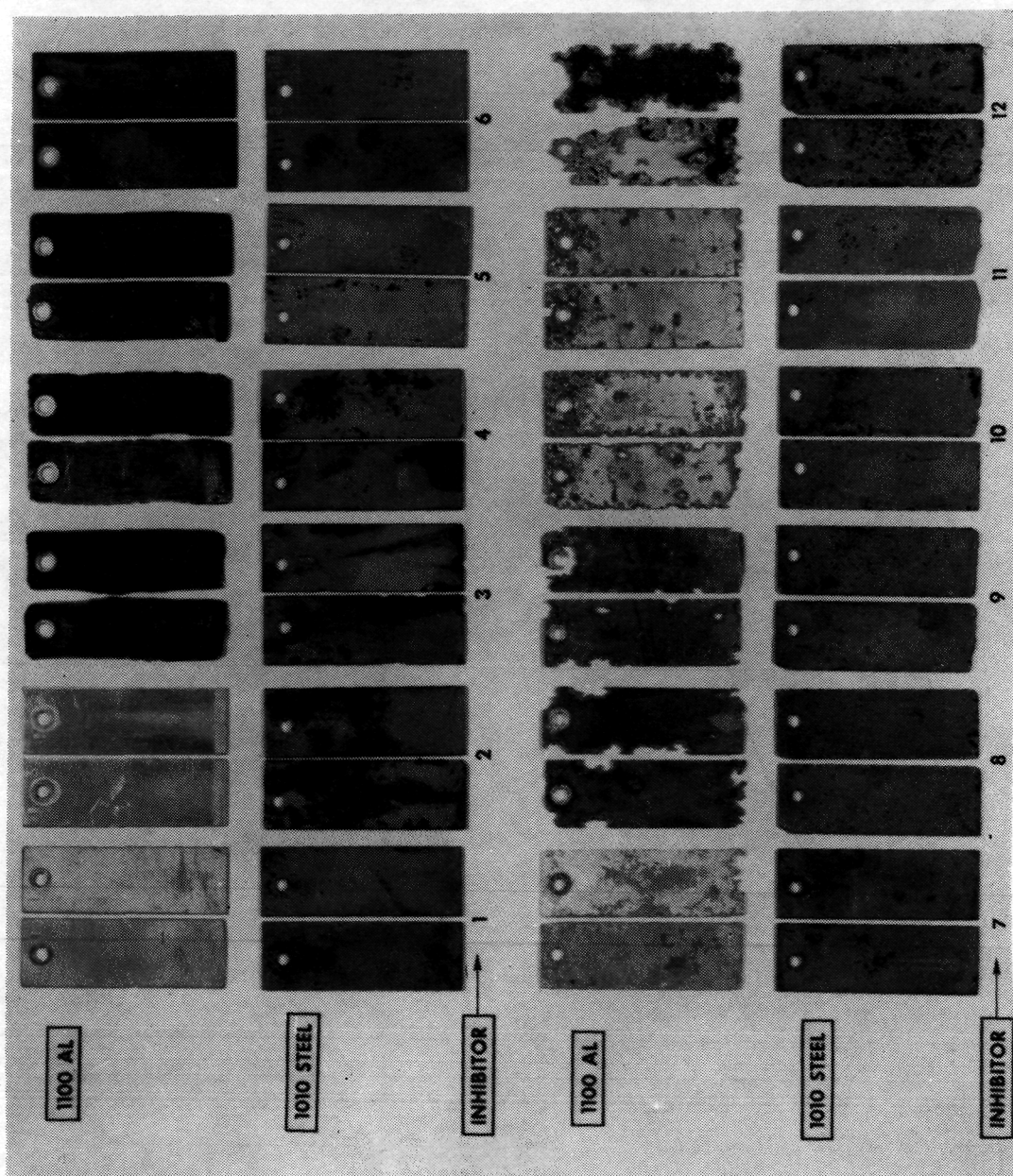


Figure 2. Appearance of test specimens.

REFERENCES

1. Humphries, T. S. and DeRamus, G. E., Jr.: Corrosion Inhibitors for Solar Heating and Cooling Systems. NASA TN D-8409, February 1977.
2. Rowe, L. C.: Corrosion Inhibitors. NACE, 173-189, 1973.

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| 16. ABSTRACT This is a continuation of the test program, that was previously reported (NASA TN D-8409, February 1977), to find suitable and effective inhibitors for solar heating and cooling systems. Inhibitors which appeared promising in the previous tests and additional inhibitors including several proprietary products were selected for evaluation. Evaluation of the inhibitors was based on corrosion protection afforded an aluminum-mild steel-copper-stainless steel assembly in a hot corrosive water. Two inhibitors were found to be effective and show promise for protecting multimetallic solar heating systems. | | | |
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